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Extraction Studies in the Platinum Metals Group.

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EXTRACTION STUDIES IN THE PLATINUM METALS GROUP

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He would also like to express his deepest appreciation for the encouragement and assistance of his wife Patricia H. Senn and his mother Etta H. Woest.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The aim of this research was to affect separations in the platinum metals group utilizing extraction methods. Osmium and ruthenium were excluded since they are easily separated from platinum, palladium, rhodium and iridium as the volatile tetroxides.

The distribution coefficients for platinum, palladium, rhodium and iridium were measured in a hydrochloric acid-sodium chloride-tributyl phosphate system and a potassium thiocyanate-tributyl phosphate system. The variations of distribution coefficients with molarity of hydrochloric acid were studied in the chloride system. The variations of distribution coefficients with the mole ratio of potassium thiocyanate to metal and the pH were investigated in the extraction of the metal thiocyanate complexes.

A comparison of separations that might be affected in the chloride system with those that might be affected in the thiocyanate system was made. On the basis of this comparison, the chloride system was utilized in the separational procedures.

Utilizing the chloride system and the principles of countercurrent distribution, the separations of iridium from rhodium, platinum from rhodium and platinum from palladium were affected. The method of Bush and Densen was used for the separation of iridium from rhodium in 6M hydrochloric acid saturated with sodium chloride. The extractant used was tributyl phosphate. The conditions for the separation

of platinum from rhodium and platinum from palladium utilized extractions from 3M hydrochloric acid saturated with sodium chloride and tributyl phosphate. The extractant used was tributyl phosphate.

The three separations affected were quantitative, simple, fast and economical.

INTRODUCTION

Extraction techniques have been utilized in the field of chemistry for many years. Until recent years most of the work done has been in the field of organic chemistry. However, the advent of atomic energy stimulated the use of this technique for separating elements closely related in their chemical properties.

Extraction as treated in this dissertation deals with the transfer of dissolved material reversibly or otherwise from one liquid phase to another liquid phase. The liquid phase in which the material is dissolved will be called the "raffinate". The "extractant" refers to the arbitrarily chosen liquid phase to which the material is to be transferred.

Extraction techniques can be classified according to the purpose for which they are used. These classifications are extraction for removal and extraction for fractionation. Frequently all that is desired in an extraction is the quantitative removal of the solute from a phase unsatisfactory for its further study. This technique is known as extraction for removal. This operation may result also in a greater or lesser degree of separation of the desired solute from other undesired solutes. If essentially none of the undesired solutes are extracted the process is greatly simplified and all that need be considered is the completeness of extraction.

Extraction for fractionation is used when it is desired to separate two or more components, all of which distribute, but in amounts

such that they exhibit different distribution coefficients. The primary impetus for the utilization of this technique for separating closely related solutes belongs to Jantzen (19) and Cornish, Archibald, Murphy and Evans (9). This work has been extended, particularly by Craig whose many reviews (10 - 15) have been quite useful. Also of great use has been the section by Craig and Craig (27) on extraction and distribution in Weissberger's Technique of Organic Chemistry.

The theory pertaining to the extraction of inorganic solutes postulates the formation of an uncharged complex which is the species extracted. This uncharged complex may form in two ways; coordination or ion association. As an example of the uncharged complex formed by coordination, the formation of metal chelates is probably the best. When metal chelates are to be extracted, the technique most widely used is that of extraction for removal. In most cases this is quite satisfactory since a great deal of specificity may be obtained by adjusting experimental conditions. As opposed to this, the extraction of an uncharged complex formed by ion association rarely shows any degree of specificity, particularly when the species to be extracted are closely related in chemical properties. As a result of this relatively non-specific phenomenon, most extraction separations involving ion association behavior are carried out by extraction for fractionation.

Solvent extraction as a method for affecting separations in the platinum group metals has not been widely used as can be seen in the review by McBryde (22). Irving (18) in his review of extraction and its application to inorganic analysis has noted that of the

six platinum group metals only 5% iridium and traces of platinum are extracted by ether from 6N hydrochloric acid. Discussing the role of extraction in analytical chemistry, Morrison (25) notes also that osmium is completely extracted from bromide solutions. Further, Morrison's section on extraction of coordination types lists platinum and palladium extracting as the dithozonates. Palladium can be extracted as the oxinate.

In recent articles involving extraction of ion association systems tributyl phosphate has been reported to be a highly successful extractant. In these articles Aven and Freiser (1) and Melnick, Freiser and Beeghly (24) reported the extraction of the iron thiocyanate complex and Melnick and Freiser (23) the extraction of the copper thiocyanate complex. Since tributyl phosphate is commercially available, nonvolatile and noninflammable, it offers many advantages over extractants presently being used.

The aim of this research work was to develop separations in the platinum group metals. In recent years a great deal of work has been done in this area, particularly in the field of ion exchange (6, 8, 20, 21). However, the field of extraction, in which little work has been done, offers many advantages. In general an extraction is faster, simpler and more economical than ion exchange separations. In carrying out the aim of this research work the metals studied were platinum, palladium, rhodium and iridium. Osmium and ruthenium were not included since they are easily separated from the other platinum metals by virtue of the volatility of their tetroxides. Extractions of the four metals as the chloride complexes and as the

thiocyanate complexes were studied. As a result of these studies separations for rhodium and iridium, rhodium and platinum and platinum and palladium were affected utilizing countercurrent distribution techniques.

EXPERIMENTAL

(A) Preparation of Solutions

Platinum thermocouple wire was used for preparation of the standard platinum solution. Initially, 1.3374 g. of platinum were dissolved in aqua-regia. The solution was then evaporated to dryness and taken up in concentrated hydrochloric acid. The solution was again evaporated to dryness and taken up in concentrated hydrochloric acid. This procedure was repeated two more times in order to destroy any nitrosyl chloroplatinic chloride which was formed during dissolution. Finally the residue was taken up in 100 ml. of concentrated hydrochloric acid and diluted to one liter. The concentration of the stock solution was then 1337.4 ppm. platinum. When this supply of platinum was exhausted a new solution containing 1.0306 g. of platinum thermocouple wire was prepared following the aforementioned procedure. The concentration of the new stock solution was 1030.6 ppm. platinum.

The palladium stock solution was prepared by dissolving 1.0000 g. of palladium metal in fuming perchloric acid. The solution was fumed to dryness, taken up in 100 ml. of conecntrated hydrochloric acid and diluted to one liter. The solution was standardized using the dimethylglyoxime procedure from Hillebrand and Lundell (17). The concentration of the new stock solution was 1000 ppm. palladium. When this supply of palladium was exhausted a new solution containing

approximately 1.85 g. of palladium metal was made up by the aforementioned procedure. The concentration was found by the standardization to be 1849 ppm. palladium.

The rhodium stock solution was prepared by dissolving rhodium (III) chloride from A. D. Mackay, Inc., in 100 ml. of concentrated hydrochloric acid. The solution was then diluted to one liter. The stock solution of rhodium was standardized by spectrophotometric analysis using the method of Ayres and Young (5). The standard curve for the procedure had been prepared from a rhodium solution standardized by the method of Gilchrist (16).

The iridium stock solution was prepared by dissolving iridium (IV) chloride from A. D. Mackay, Inc., in 100 ml. of concentrated hydrochloric acid. The solution was then diluted to one liter. The stock solution of iridium was standardized by spectrophotometric analysis using the method of Ayres and Quick (3). The standard curve for the procedure had been prepared from an iridium solution standardized by the method of Gilchrist (16).

The various hydrochloric acid solutions used in all cases were 37% C. P. hydrochloric acid or an appropriate dilution thereof. The sodium chloride used was reagent grade.

The tributyl phosphate used was obtained from Mathieson, Coleman and Bell and was used without further purification.

The potassium thiocyanate used was reagent grade and was added by weight to give the correct mole ratios.

The buffer solutions used were prepared according to specifications of Clark and Lubs found in the Handbook of Chemistry by Lange.

For a pH = 1, the buffer solution was prepared by mixing 485 ml. of 0.2M hydrochloric acid with 250 ml. of 0.2M potassium chloride and diluting to one liter. A pH = 2 buffer solution was prepared by mixing together 53 ml. of 0.2M hydrochloric acid and 250 ml. of 0.2M potassium chloride and diluting to one liter. The pH = 3 buffer system was prepared by mixing together 203 ml. of 0.1M hydrochloric acid and 500 ml. of 0.1M potassium acid phthalate and diluting to one liter. For the pH = 3.8 buffer solution, 26.3 ml. of 0.1M hydrochloric acid were mixed with 500 ml. of 0.1M potassium acid phthalate and diluted to one liter.

(B) Apparatus

A Beckman Model DU spectrophotometer with matching silica cells was used for the analysis of the platinum, palladium, rhodium and iridium solutions.

The countercurrent distribution apparatus used was the extraction machine built and assembled by Ryland (26).

The measurement of distribution coefficients utilized an eight tube Virtis extractomatic apparatus.

(C) Analytical Procedures

The platinum solutions were analyzed by the method of Ayres and Meyer (2). In the analysis for platinum, aqua-regia was added and the sample was evaporated to a moist residue. Concentrated hydrochloric acid was added and the sample again evaporated to a moist residue. The sample was then taken up in approximately 10% hydrochloric acid for analysis. To the sample were added 10.00 ml. of concentrated

hydrochloric acid, 25.0 ml. of 20% ammonium chloride and 20.0 ml. of 1.0 molar tin (II) chloride solution. The sample was then diluted to 100.0 ml. and allowed to stand for thirty minutes. The per cent. absorbancy was read at 403 mμ.

The palladium solutions were analyzed by the method of Ayres and Tuffly (4). The initial step in the analysis of a sample for palladium was to fume the sample down with a mixture of 95 parts perchloric acid to 5 parts nitric acid. The sample was then dissolved in concentrated hydrochloric acid and taken down to a moist residue. The sample was then dissolved in 3% hydrochloric acid. To the sample, 5.0 ml. of 48% hydrobromic acid was added. The sample was diluted to 25.0 ml. and allowed to stand for thirty minutes. The per cent. absorbancy was read at 505 mμ.

The rhodium solutions were analyzed by the method of Ayres and Young (5). The rhodium sample was evaporated to a moist residue after addition of aqua-regia. The moist residue was dissolved in concentrated hydrochloric acid and evaporated to dryness. The sample was dissolved in 3% hydrochloric acid. To the sample 10.0 ml. of a sodium acetate-acetic acid buffer system and 50.0 ml. of a 5% sodium hypochlorite solution were added. The sample was diluted to 100.0 ml. and allowed to stand one hour. The per cent. absorbancy was read at 665 mμ.

The iridium solutions were analyzed by the method of Ayres and Quick (3). The iridium sample was evaporated to a moist residue after addition of aqua-regia. The moist residue was dissolved in 10% hydrochloric acid. To the sample mixed acids--50 parts perchloric

acid, 50 parts phosphoric acid, 5 parts nitric acid--were added and the samples heated at 110° - 120° C. for one hour. The temperature was then raised to 150° - 160° C. and heated approximately eight minutes in excess of the time necessary for a purple color to develop. The sample was then diluted to 25.0 ml. with 1% nitric acid. The per cent. absorbancy was read at 564 mμ. The data for the standard curves may be seen in tables I, II, III, and IV and the standard curves may be seen in figures I, II, III and IV.

In cases where the sample to be analyzed contained an appreciable amount of potassium thiocyanate, a preliminary oxidation was carried out by adding 5 ml. of concentrated nitric acid. The sample at first turned dark brown and then with a sudden evolution of gases it turned a bluish-green color. The samples thus treated were not heated until the bluish-green color appeared.

TABLE I

Data for Platinum Standard Curve

Platinum Concentration (ppm)	% A
1.34	15.0
2.67	24.9
5.35	41.8
10.7	64.1
21.4	86.3
26.7	92.0

TABLE II

Data for Palladium Standard Curve

Palladium Concentration (ppm)	% A
40	26.0
80	46.0
160	71.0
200	79.0
300	90.5

TABLE III

Data for Rhodium Standard Curve

Rhodium Concentration (ppm)	% A
2.4	22.0
5.7	40.0
7.8	50.0
13.0	69.8
26.0	89.5

TABLE IV

Data for Iridium Standard Curve

Iridium Concentration (ppm)	% A
6.1	18.1
20.2	50.5
40.5	73.0
61.0	89.0
81.0	94.5

FIGURE I

Standard Curve for Platinum

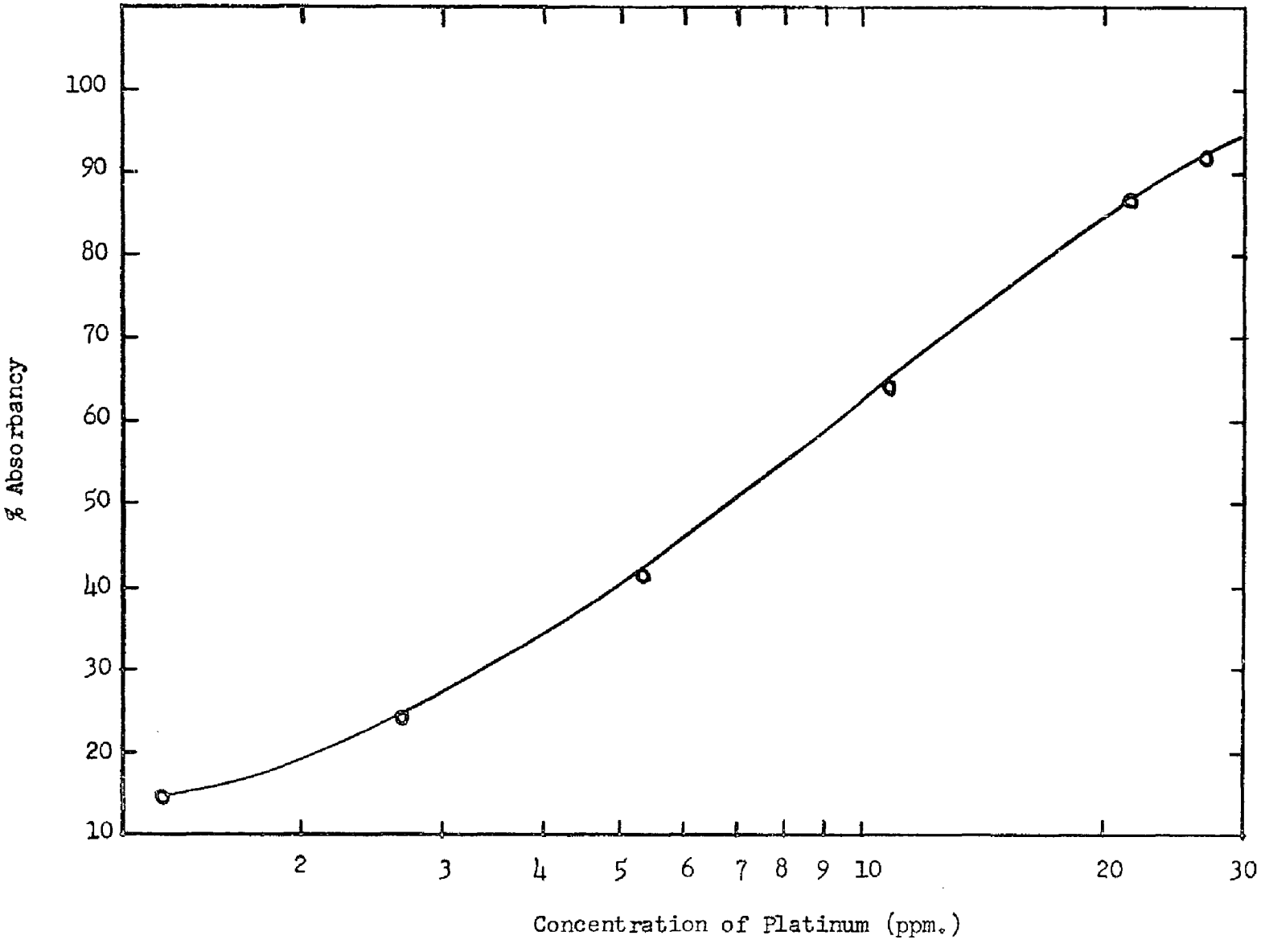


FIGURE II

Standard Curve for Palladium

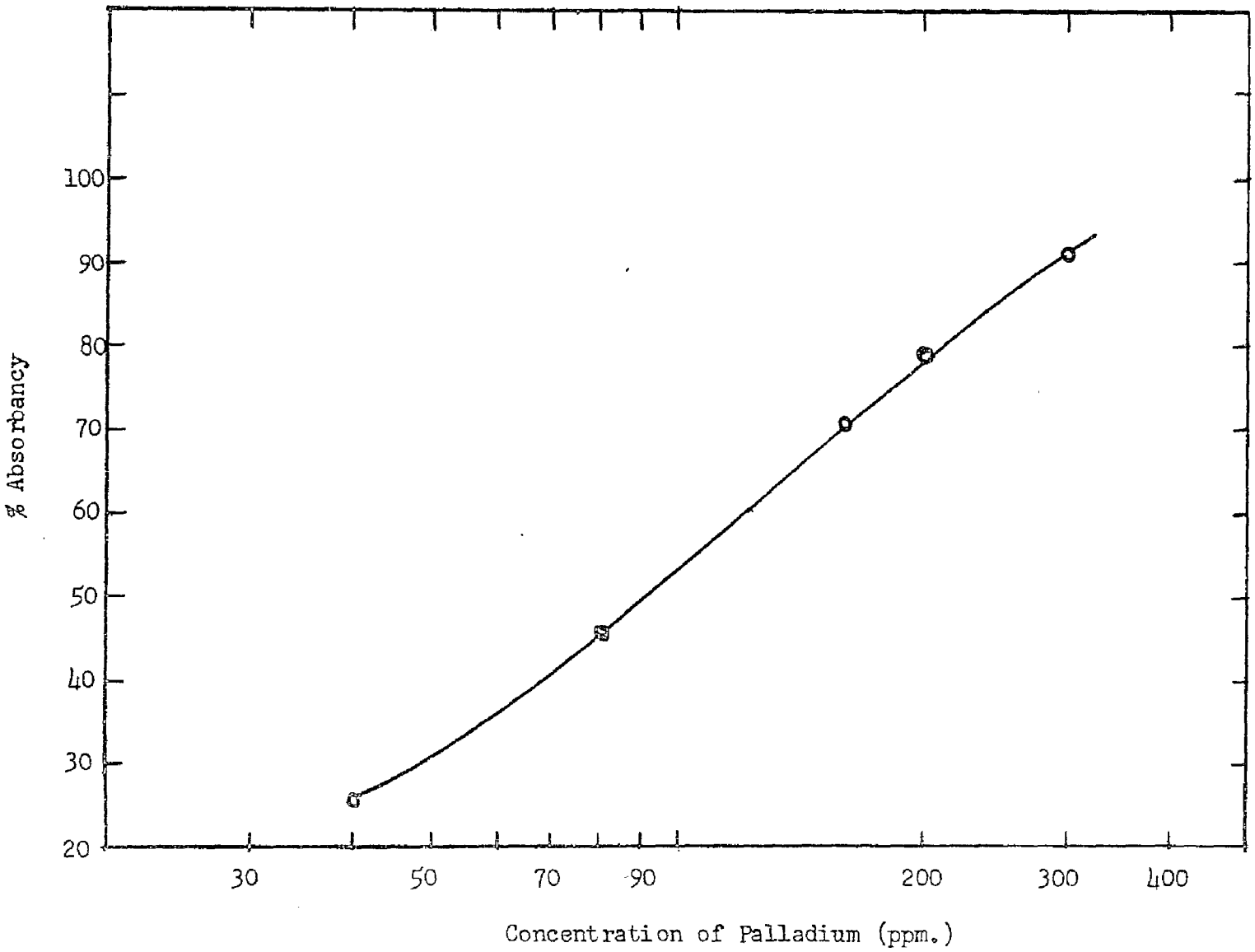


FIGURE III

Standard Curve for Rhodium

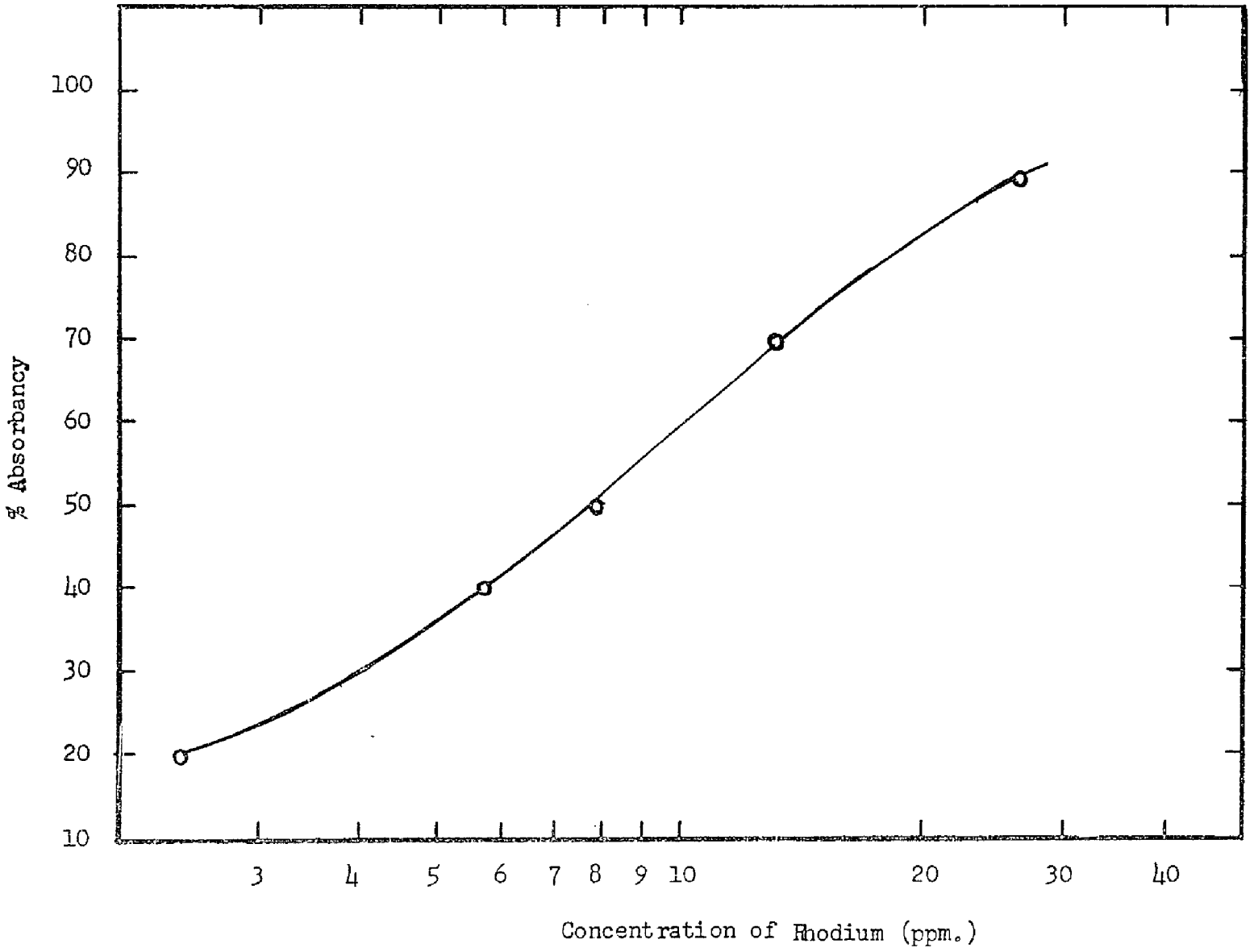
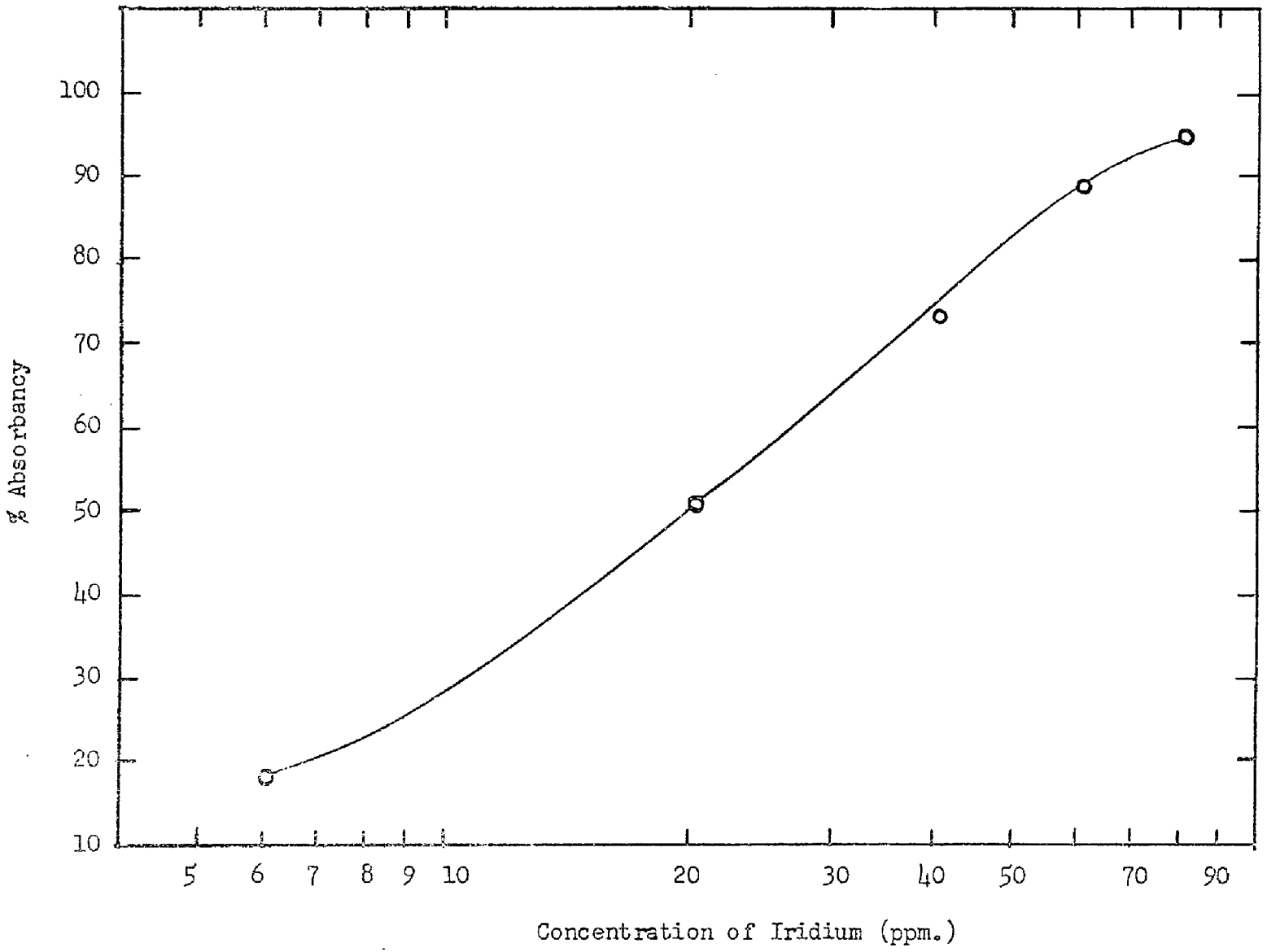


FIGURE IV

Standard Curve for Iridium



(D) Measurement of Distribution Coefficients

(1) Hydrochloric Acid - Sodium Chloride - Tributyl Phosphate System

The procedures followed for measuring the distribution coefficients of the chloro complexes of platinum, palladium, rhodium and iridium were identical, hence the procedure described below applies to all four cases.

Six 5.00 ml. aliquots of the stock sample solution were taken to dryness on the steam bath. The samples were then dissolved in appropriate amounts of concentrated hydrochloric acid such that on dilution to 15 ml. the molar concentration of the hydrochloric acid in the six samples was 1, 2, 3, 5, 7, and 9. The systems were then saturated with sodium chloride. Ten ml. of tributyl phosphate were then added to the system and the two phases were equilibrated for one minute on a Virtis extractomatic device.

The raffinate was then filtered through Whatman #1 filter paper. This eliminated the contamination of the raffinate by the extractant, as the extractant could not pass through the wet Whatman #1 filter paper. The raffinate was then analyzed by the procedure previously described in the Analytical Section.

The data collected in these experiments may be seen in tables V, VI, VII and VIII. A graphical picture of the variation of the distribution coefficient with molarity of hydrochloric acid may be seen in figure V. The distribution coefficient is defined as:

$$K_d = \frac{\text{mg. metal/ ml. of extractant}}{\text{mg. metal/ ml. of raffinate}}$$

TABLE V

Extraction of Platinum
from Hydrochloric Acid-Sodium Chloride Systems

Sample	HCl Concentration (M)	mg. Pt Taken	mg. Pt in Raffinate	mg. Pt in Extractant	$^*K_d$
1	1	6.69	4.01	2.68	1.00
2	2	6.69	1.81	4.88	4.06
3	3	6.69	0.47	6.22	13.20
4	5	6.69	0.47	6.22	13.20
5	7	6.69	0.47	6.22	13.20
6	9	6.69	0.67	6.02	9.00

$$^*K_d = \frac{\text{mg. Pt/ml. of Extractant}}{\text{mg. Pt/ml. of Raffinate}}$$

TABLE VI

Extraction of Palladium
from Hydrochloric Acid-Sodium Chloride Systems

Sample	HCl Concentration (M)	mg. Pd Taken	mg. Pd in Raffinate	mg. Pd in Extractant	$^*K_d$
1	1	5.00	4.71	0.29	0.09
2	2	5.00	4.00	1.00	0.37
3	3	5.00	4.05	0.95	0.35
4	5	5.00	3.81	1.19	0.45
5	7	5.00	3.81	1.19	0.45
6	9	5.00	3.90	1.10	0.42

$$^*K_d = \frac{\text{mg. Pd/ml. of Extractant}}{\text{mg. Pd/ml. of Raffinate}}$$

TABLE VII

Extraction of Rhodium
from Hydrochloric Acid-Socium Chloride Systems

Sample	HCl Concentration (M)	mg. Rh Taken	mg. Rh in Raffinate	mg. Rh in Extractant	$^*K_d$
1	1	3.70	3.70	0.00	0.00
2	3	3.70	3.35	0.35	0.16
3	5	3.70	3.11	0.59	0.29
4	7	3.70	3.11	0.59	0.29
5	9	3.70	3.11	0.59	0.29

$$^*K_d = \frac{\text{mg. Rh/ml. of Extractant}}{\text{mg. Rh/ml. of Raffinate}}$$

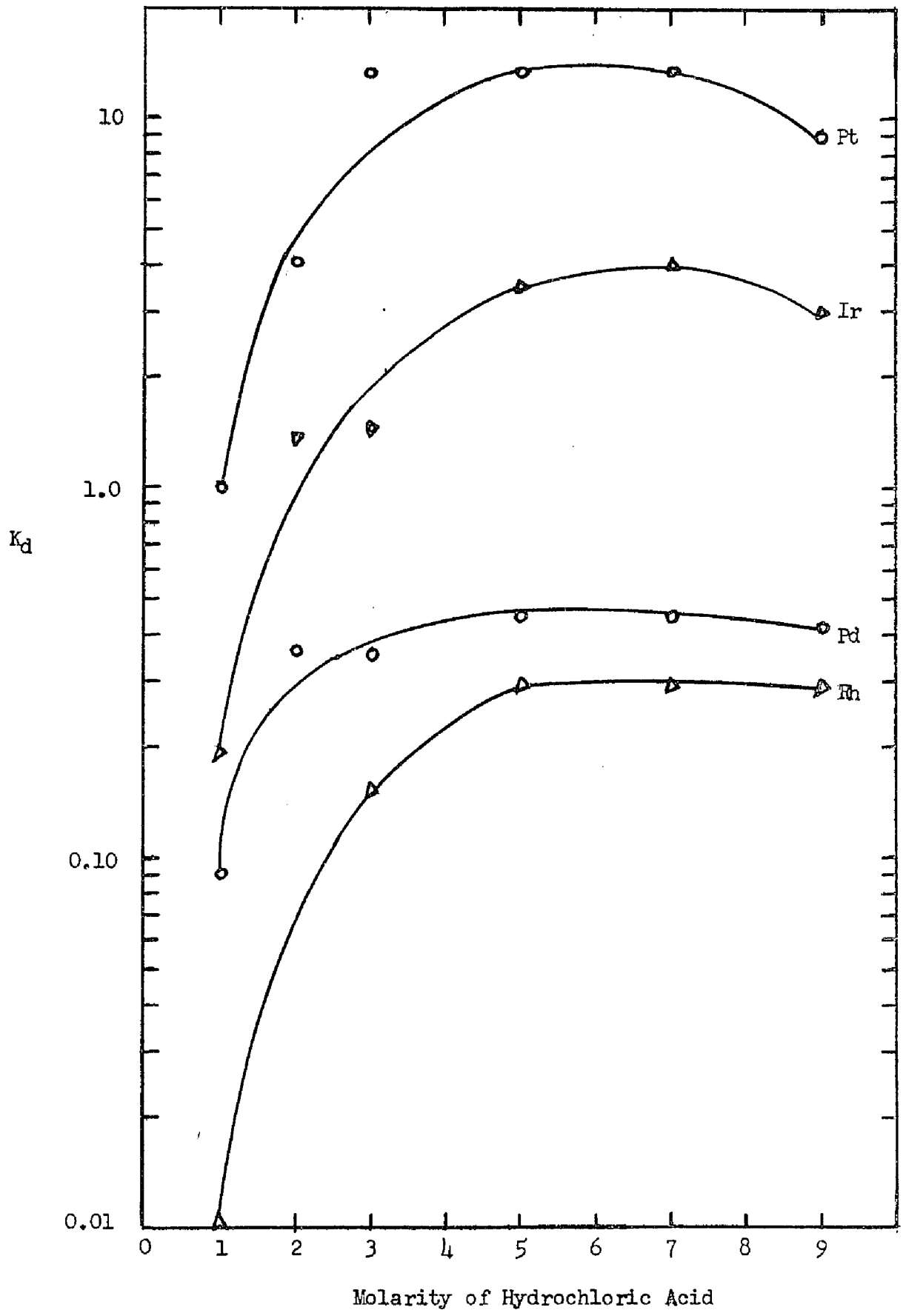
TABLE VIII

Extraction of Iridium
from Hydrochloric Acid-Sodium Chloride Systems

Sample	HCl Concentration (M)	mg. Ir Taken	mg. Ir in Raffinate	mg. Ir in Extractant	*K_d
1	1	2.66	2.36	0.30	0.19
2	2	2.66	1.39	1.27	1.37
3	3	2.66	1.36	1.30	1.43
4	5	2.66	0.79	1.87	3.53
5	7	2.66	0.72	1.94	4.04
6	9	2.66	0.89	1.77	3.00

$$*K_d = \frac{\text{mg. Ir/ml. of Extractant}}{\text{mg. Ir/ml. of Raffinate}}$$

FIGURE V


10
1.0
0.10
0.01
K_d
Pt
Ir
Pd
Rh
0
1
2
3
4
5
6
7
8
9
Molarity of Hydrochloric Acid

(2) Potassium Thiocyanate - Tributyl Phosphate System

The extractions of platinum, palladium, rhodium and iridium were run at pH's of 1, 2, 3 and 3.8 with mole ratios of potassium thiocyanate to metal of 10:1 and 500:1 at each pH. The procedures in each case were the same and the procedure described below applies to all four cases. Platinum, palladium and rhodium were run in duplicate. Iridium was not.

Eight 5.00 ml. aliquots of the stock sample solution were taken to dryness on a steam bath. The samples were then dissolved in the appropriate buffer solutions such that there were two samples at each pH. Solid potassium thiocyanate was added so that at each pH there was a 10:1 and a 500:1 mole ratio of potassium thiocyanate to metal. The samples were then heated fifteen minutes on a steam bath and allowed to cool. The samples were transferred to the extraction tubes and diluted to 35 ml. with the appropriate buffer solution.

Next, 25 ml. of tributyl phosphate were added and the system equilibrated for one minute on the Virtis extractomatic apparatus. The raffinate was filtered through Whatman #1 filter paper and taken for analysis by the aforementioned procedures in the Analytical Section.

The results can be seen in tables IX, X, XI and XII. The variation of the distribution coefficient with pH at a 10:1 mole ratio may be seen in figure VI and for a 500:1 mole ratio in figure VII.

The results from the chloride system indicated that there was a possibility of separating platinum from rhodium, iridium from rhodium, platinum from palladium and iridium from palladium.

TABLE IX

Extraction of Platinum from Potassium Thiocyanate Systems

Series #1

Sample	pH	KSCN:Pt Ratio	mg. Pt Taken	mg. Pt in Raffinate	mg. Pt in Extractant	*K_d
1	1.0	10:1	5.153	0.113	5.040	62.2
2	1.0	500:1	5.153	0.113	5.040	62.2
3	2.0	10:1	5.153	0.113	5.040	62.2
4	2.0	500:1	5.153	0.113	5.040	62.2
5	3.0	10:1	5.153	1.253	3.900	42.4
6	3.0	500:1	5.153	0.113	5.040	62.2
7	3.8	10:1	5.153	1.403	3.750	40.1
8	3.8	500:1	5.153	0.113	5.040	62.2

Series #2

Sample	pH	KSCN:Pt Ratio	mg. Pt Taken	mg. Pt in Raffinate	mg. Pt in Extractant	*K_d
1	1.0	10:1	5.153	0.113	5.040	62.2
2	1.0	500:1	5.153	0.113	5.040	62.2
3	2.0	10:1	5.153	0.113	5.040	62.2
4	2.0	500:1	5.153	0.113	5.040	62.2
5	3.0	10:1	5.153	1.073	4.080	53.3
6	3.0	500:1	5.153	0.113	5.040	62.2
7	3.8	10:1	5.153	1.443	3.710	40.1
8	3.8	500:1	5.153	0.113	5.040	62.2

$$*K_d = \frac{\text{mg. Pt/ml. of Extractant}}{\text{mg. Pt/ml. of Raffinate}}$$

TABLE X

Extraction of Palladium from Potassium Thiocyanate Systems

Series #1

Sample	pH	KSCN:Pd Ratio	mg. Pd Taken	mg. Pd in Raffinate	mg. Pd in Extractant	*K_d
1	1.0	10:1	9.245	0.000	9.245	
2	1.0	500:1	9.245	0.175	9.070	72.6
3	2.0	10:1	9.245	0.145	9.100	87.9
4	2.0	500:1	9.245	0.195	9.050	65.1
5	3.0	10:1	9.245	0.325	8.920	38.5
6	3.0	500:1	9.245	0.165	9.080	77.0
7	3.8	10:1	9.245	0.395	8.850	31.3
8	3.8	500:1	9.245	0.125	9.120	102

Series #2

Sample	pH	KSCN:Pd Ratio	mg. Pd Taken	mg. Pd in Raffinate	mg. Pd in Extractant	*K_d
1	1.0	10:1	9.245	0.085	9.160	150
2	1.0	500:1	9.245	0.135	9.110	94.3
3	2.0	10:1	9.245	0.115	9.130	111
4	2.0	500:1	9.245	0.175	9.070	72.6
5	3.0	10:1	9.245	0.315	8.930	39.6
6	3.0	500:1	9.245	0.195	9.050	65.0
7	3.8	10:1	9.245	0.365	8.880	34.1
8	3.8	500:1	9.245	0.175	9.070	72.6

$$*K_d = \frac{\text{mg. Pd/ml. of Extractant}}{\text{mg. Pd/ml. of Raffinate}}$$

TABLE XI

Extraction of Rhodium from Potassium Thiocyanate Systems

Series #1

Sample	pH	KSCN:Rh Ratio	mg. Rh Taken	mg. Rh in Raffinate	mg. Rh in Extractant	*K_d
1	1.0	10:1	3.70	3.60	0.10	0.038
2	1.0	500:1	3.70	0.09	3.61	56.2
3	2.0	10:1	3.70	3.46	0.24	0.097
4	2.0	500:1	3.70	0.09	3.61	56.2
5	3.0	10:1	3.70	2.82	0.88	0.435
6	3.0	500:1	3.70	0.09	3.61	56.2
7	3.8	10:1	3.70	2.19	1.51	0.966
8	3.8	500:1	3.70	0.09	3.61	56.2

Series #2

Sample	pH	KSCN:Rh Ratio	mg. Rh Taken	mg. Rh in Raffinate	mg Rh in Extractant	*K_d
1	1.0	10:1	3.70	3.26	0.44	0.86
2	1.0	500:1	3.70	0.09	3.61	56.2
3	2.0	10:1	3.70	3.16	0.54	0.236
4	2.0	500:1	3.70	0.09	3.61	56.2
5	3.0	10:1	3.70	2.58	1.12	0.609
6	3.0	500:1	3.70	0.09	3.61	56.2
7	3.8	10:1	3.70	2.24	1.46	0.910
8	3.8	500:1	3.70	0.09	3.61	56.2

$$*K_d = \frac{\text{mg. Rh/ml. of Extractant}}{\text{mg. Rh/ml. of Raffinate}}$$

TABLE XII

Extraction of Iridium from Potassium Thiocyanate Systems

Series #1

Sample	pH	KSCN:Ir Ratio	mg. Ir Taken	mg. Ir in Raffinate	mg. Ir in Extractant	*K_d
1	1.0	10:1	2.66	2.50	0.16	0.09
2	1.0	500:1	2.66	2.45	0.21	0.11
3	2.0	10:1	2.66	2.63	0.03	0.01
4	2.0	500:1	2.66	1.85	0.81	0.61
5	3.0	10:1	2.66	1.69	0.97	0.81
6	3.0	500:1	2.66	1.63	1.03	0.88
7	3.8	10:1	2.66	1.38	1.28	1.29

$$*K_d = \frac{\text{mg. Ir/ml. of Extractant}}{\text{mg. Ir/ml. of Raffinate}}$$

FIGURE VI

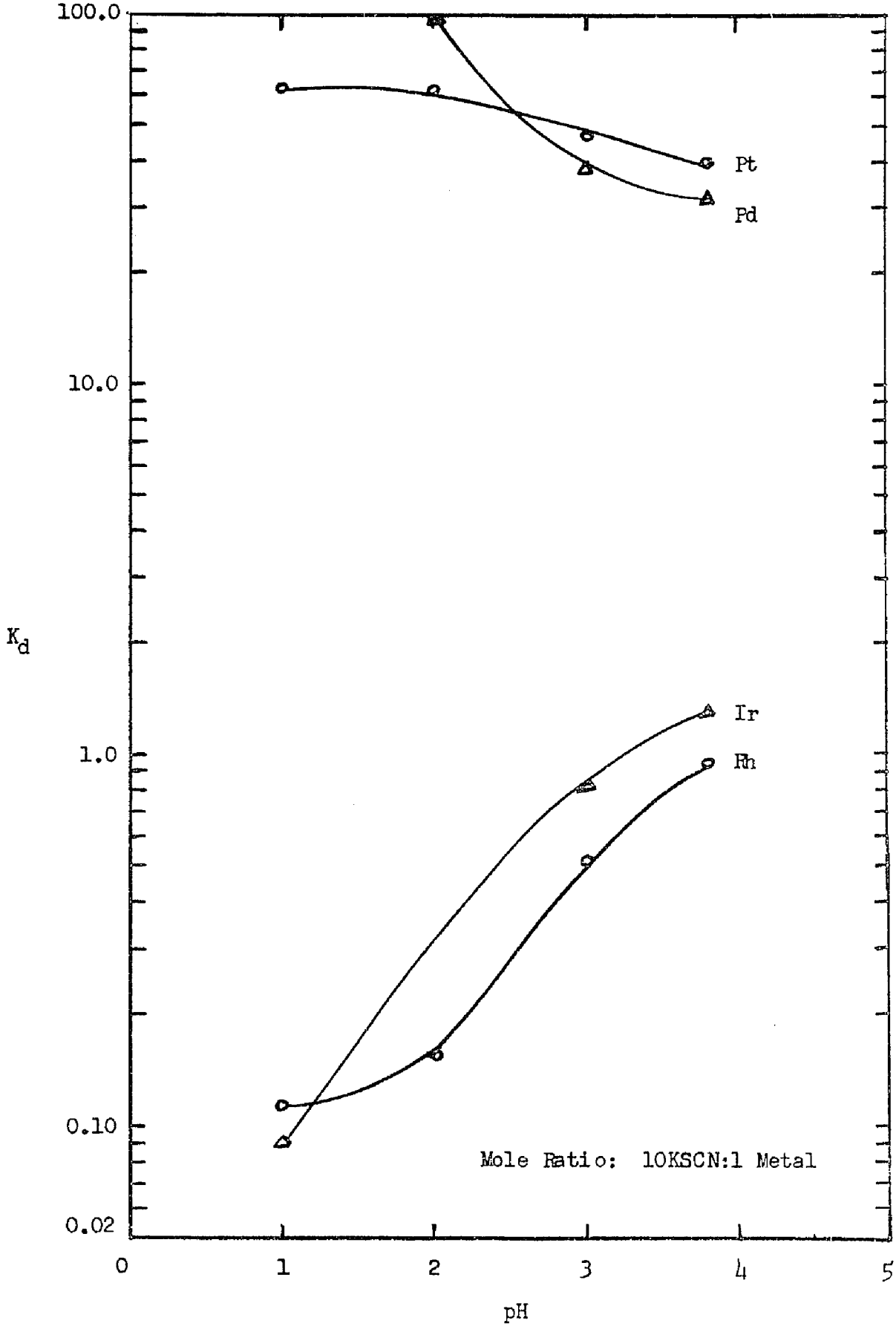
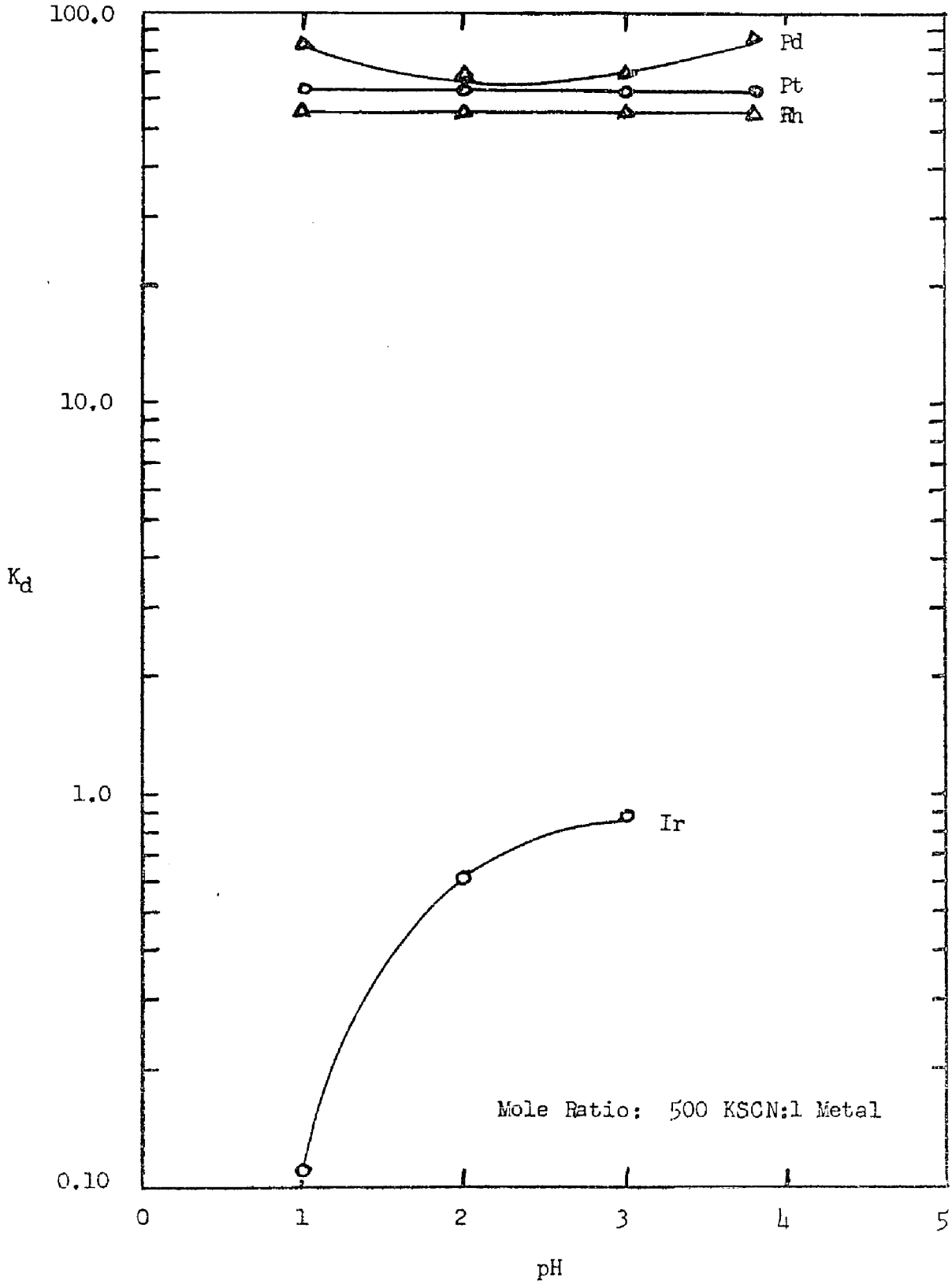

100.0
10.0
1.0
0.10
0.02
K_d
Pt
Pd
Ir
Rh
Mole Ratio: 10KSCN:1 Metal
0
1
2
3
4
5
pH

FIGURE VII


100.0
10.0
1.0
0.10
K_d
Pd
Pt
Rh
Ir
Mole Ratio: 500 KSCN:1 Metal
0
1
2
3
4
5
pH

Considering first the results from the 10:1 mole ratio of potassium thiocyanate to metal, there appeared to be a possibility of separating platinum from rhodium or iridium and palladium from rhodium or iridium.

The results from the 500:1 mole ratio of potassium thiocyanate to metal indicated the possibility of separating platinum, palladium and rhodium from iridium.

A comparison of the two systems from a practical standpoint produced the fact that the chloride is far superior. Not only does it possess the advantage of being simpler but also that of being faster. Hence any separation that can be affected by either system would preferably be developed using the chloride system. As a result of these considerations it was decided to work on the separations of platinum from rhodium, rhodium from iridium and platinum from palladium in the chloride system. The data in the thiocyanate systems indicated the possibility of separating platinum from iridium and rhodium from iridium. The consideration of the separation of rhodium from iridium in the thiocyanate system was stimulated by difficulties in the chloride system which required a manual pseudo-countercurrent process in order to affect the separation. The separation of iridium from palladium in either system was not considered since the existing methods of separation are adequate.

(E) Separation of Rhodium and Iridium

(1) Theoretical Section

The extraction technique used for the separation of rhodium and iridium was that of Bush and Densen (7). For the development of simple distribution curves the following definitions and assumptions were made:

(a) A substance in solution can be distributed between two immiscible liquid phases, x and y, such that at equilibrium

$$K_d = \frac{\text{mg. of A per ml. of x}}{\text{mg. of A per ml. of y}}$$

Furthermore it was assumed that in working with dilute solutions the distribution coefficient, K_d, did not vary with concentration.

(b) It was assumed that the solutes under consideration were neither associated nor dissociated appreciably in either solvent.

(c) The conditions of equilibrium were assumed to be constant.

(d) There was only negligible adsorption of solute on the apparatus or at the liquid-liquid interface.

If the total volumes of the two solvents are designated as V_x and V_y respectively, and P_a represents the fraction of solute A which is in the solvent x at equilibrium ($1 - P_a$, the remainder of A, is in the solvent y), then

Total amount of A in x = (mg. per ml. of x) V_x

Total amount of A in y = (mg. per ml. of y) V_y

$$\text{and } \frac{P_a}{1 - P_a} = \frac{(\text{mg. per ml. of x})V_x}{(\text{mg. per ml. of y})V_y} = K_d \frac{V_x}{V_y}$$

By transposing and combining appropriate terms

$$P_a = \frac{K_a V_x}{K_a V_x + V_y}$$

The fraction of solute A in solvent Y is Q_a where $Q_a = 1 - P_a$.

In dealing with mixtures of solutes it is assumed that each solute distributes independantly. It was on this assumption that the theoretical curves were calculated. This assumption is not strictly true but the deviations must be determined experimentally, as there is no method for calculating this interaction.

Using the equations derived and the assumptions made the calculation of the distribution of each solute of the mixture was made. Actually the system used for separating rhodium and iridium did not obey all of the assumptions. Probably the worst assumption was (b) which was not considered to be applicable to the ion association system studied.

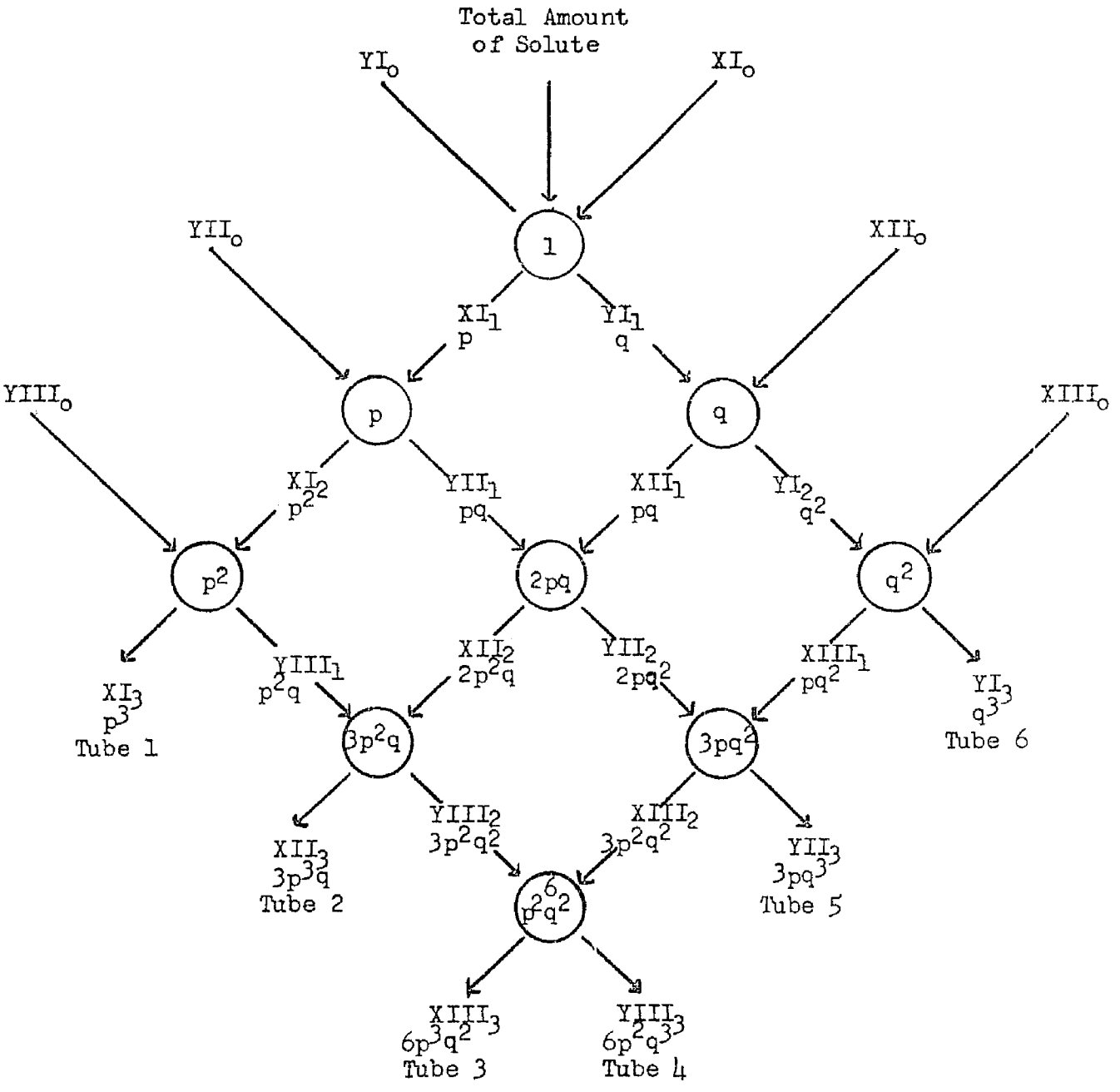
The extraction pattern and the algebraic calculation of the fraction of the solute in each of these solutions was carried out as shown in figure VIII, where: (1) the combinations and separations were carried out as directed by the arrows; (2) the circled terms represented the fractional amounts of a single solute combined and equilibrated between the two phases in a separatory funnel; (3) the two terms below an equilibration were obtained by adding, the two terms above the equilibration, and multiplying by p for the x term below and by Q for the y term below.

In dealing with separation of rhodium and iridium, the volume ratio of extractant to raffinate can be calculated from

$$\frac{K_{d1}V_x}{K_{d1}V_x + V_y} = 1 - \frac{K_{d2}V_x}{K_{d2}V_x + V_y}$$

FIGURE VIII

Extraction Pattern of Bush and Densen



which can be simplified to

$$\frac{V_x}{V_y} = \sqrt{\frac{1}{K_{d_1} K_{d_2}}}$$

(2) Experimental Section

In the separation of rhodium and iridium 5.00 ml. aliquots of a 532 ppm. iridium solution and 740 ppm. rhodium solution were mixed for the separation. Four separate runs were made. The standardized procedure is as follows:

The sample containing the mixture of rhodium and iridium was evaporated to dryness on a steam bath. The sample was then dissolved in 6M hydrochloric acid saturated with sodium chloride. One ml. of hydrogen peroxide was added and the solution boiled vigorously. The sample solution was cooled, transferred to a separatory funnel and diluted to 15 ml. with the hydrochloric acid-sodium chloride mixture. The sample solution was then equilibrated with 14 ml. of tributyl phosphate. The extractions were carried out using the extraction pattern of Bush and Densen (7) shown in figure VIII. However, the original raffinate had to be oxidized with hydrogen peroxide each time it was extracted in order to completely remove the iridium. Referring to figure VIII, this means raffinate solutions XI_0, XI_1 and XI_2 had to be oxidized before being contacted by extractant solutions YI_0, YII_0 and $YIII_0$. No further oxidations were needed after the three mentioned above had been accomplished.

The extractant phase was stripped by equilibrating with 15 ml. of a 25% nitric acid solution saturated with sodium nitrate. Usually three to five equilibrations were sufficient to quantitatively remove

any rhodium or iridium from the extractant phase. The analyses were carried out by the methods described in the Analytical Section.

(3) Results Section

The data for four separations may be seen in table XIII. In plotting the data the average value per tube was plotted against the tube number. The tubes were numbered in a counterclockwise direction as may be seen in figure VIII. This experimental plot is compared with the theoretical plot (dotted line) in figure IX. The data for the theoretical plot was taken from table XIV. The results of the above separations show an average recovery of 3.66 mg. of rhodium out of 3.70 mg. taken and 2.51 mg. of iridium out of 2.66 mg. taken. Although the oxidation step required before each extraction of the original raffinate was time consuming, the separation was easily carried out in one to one and one-half hours. This is considerably faster than most of the separations being used at the present time.

TABLE XIII

Data for the Separation of Rhodium and Iridium

System: Hydrochloric Acid-Sodium Chloride-Tributyl Phosphate

Quantities Taken: 2.66 mg. of Iridium and 3.70 mg. of Rhodium

	Run #1		Run #2		Run #3		Run #4	
Tube Number	mg. Rh	mg. Ir	mg. Rh	mg. Ir	mg. Rh	mg. Ir	mg. Rh	mg. Ir
0	3.35	0.00	3.56	0.00	3.66	0.00	3.56	0.00
1	0.20	0.00	0.10	0.00	tr	0.00	0.19	0.00
2	tr	0.00	tr	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.35	0.00	0.31	0.00	0.31	0.00	0.39
5	0.00	2.20	0.00	2.14	0.00	2.20	0.00	2.15

Average Recovery of Rhodium = 3.66 mg.

Average Recovery of Iridium = 2.51 mg.

TABLE XIV

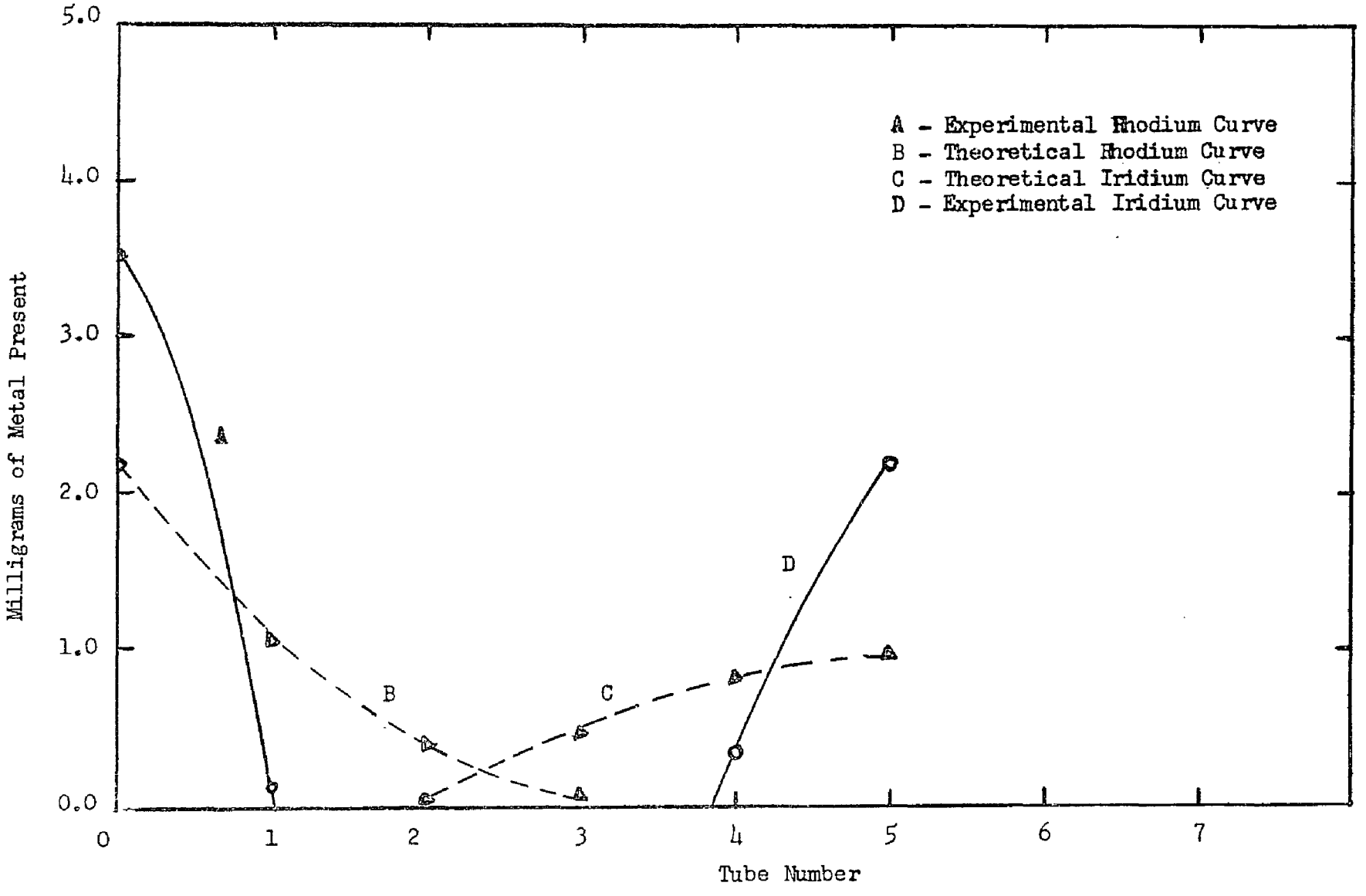
Theoretical Data for the Separation of Rhodium and Iridium

Tube Number	Fraction of Rh Present	*mg. Rh Present	Fraction of Ir Present	*mg. Ir Present
0	0.59	2.18	0.00	0.00
1	0.28	1.04	0.01	0.03
2	0.11	0.40	0.02	0.05
3	0.02	0.07	0.18	0.48
4	0.01	0.04	0.31	0.83
5	0.00	0.00	0.37	0.98

* Based on 2.66 mg. of Iridium and 3.70 mg. of Rhodium Taken for Separation

FIGURE IX

Distribution Curves for the Separation of Rhodium and Iridium



(F) Separation of Rhodium and Platinum

(1) Theoretical

In this theoretical discussion of fractionation by distribution it will be assumed that, when two solutes are extracted reversibly in a given two phase system, each will behave as if the other solute were not present. Moreover it may also be assumed that constant partition ratios are obtained over the concentration range employed.

In order to simplify the countercurrent distribution process, equal volumes of the two phases will be considered and a solute utilized which has a partition ratio of 1 in the solvent pair. Figure X, taken from Weissberger (28), illustrates this. Separate contacting tubes are arranged in a series numbered 0, 1, 2, . . . R from left to right. If a unit quantity of solute is dissolved in L_0 and V_0 moved over it, the process will be in its initial position at 0 transfer. The two phases are equilibrated and separated. Now the upper phases are shifted so that V_0 will be over L_1 and V_1 over L_0. One transfer has now been accomplished.

For the second transfer, both tubes are equilibrated and the upper layers shifted so that V_0 is over L_2, V_1 over L_1 and V_2 over L_0. Two transfers have now been accomplished and the total fraction of substance in each tube, both layers combined, is given in the table on figure X on the line opposite the number of transfers.

The table on figure X represents an expansion corresponding to $(x + y)^n = 1$, where y represents the fraction in the lower phase and x represents the fraction being transferred. The letter n corresponds

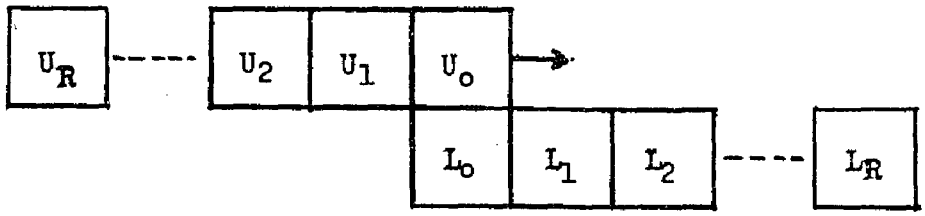
to the number of transfers. When carried out as outlined above, the amount of substance present in each tube can be calculated directly by the binomial theorem, since the fraction in the Rth tube is that of the Rth term of the binomial theorem. The fraction $T_{n,R}$ of substance present in the Rth tube after n transfers is

$$T_{n,R} = \frac{n!}{R!\ (n - R)!} \left(\frac{1}{K_d + 1}\right)^n K_d{}^R$$

This is the formula used for the theoretical calculations in the separations of rhodium from platinum and palladium from platinum.

FIGURE X

Theory of Countercurrent Distribution



Transfer No. \ Tube No.	0	1	2	3	------	R
0	1.0					
1	.50	.50				
2	.25	.50	.25			
3	.125	.375	.375	.125		
4	.0625	.25	.375	.25	.0625	
⋮						
N						

(2) Experimental Section

In the separation of rhodium and platinum, 10.00 ml. aliquots were taken from a 740 ppm. stock solution of rhodium and a 1337 ppm. stock solution of platinum. The standardized procedure was as follows:

The sample was evaporated to dryness on a steam bath and dissolved in 3M hydrochloric acid that had been previously saturated with sodium chloride and tributyl phosphate. The tributyl phosphate from this equilibration was later used as the extractant. The sample was heated ten minutes on a steam bath, cooled and transferred to the first tube in the countercurrent extractor. The other tubes in the extractor were filled with the raffinate system, 3M hydrochloric acid saturated with sodium chloride and tributyl phosphate. The final volume of the raffinate systems in the tubes was approximately 40 ml. Then 24 ml. of tributyl phosphate were added to tube 0. The system was equilibrated by inverting the tube and then allowing the system to settle. This technique was carried out twenty times for each equilibration. Then the extractant phase was transferred to tube 1 and fresh extractant added to tube 0. This procedure was repeated until the initial extractant had been transferred to tube 5, at which point the separation had been affected. The raffinate phase in each tube was then combined with the stripping solution from the respective extractant phase. The extractant phase was stripped by equilibrating with a 25% solution of nitric acid saturated with sodium nitrate. Usually, three equilibrations resulted in quantitative removal. The analytical procedures were then carried out as described in the Analytical Section.

(3) Results Section

The separation using the standardized procedure was carried out four times. The data from these four separations may be seen in table XV. The average recovery per tube is plotted against tube number in figure XI. The dotted curve is a plot of the theoretical data taken from table XVI. The average recovery of rhodium was 7.42 mg. of the 7.40 mg. taken and of platinum, 12.64 mg. of the 13.38 mg. taken.

TABLE XV

Data for the Separation of Platinum and Rhodium

System: Hydrochloric Acid-Sodium Chloride-Tributyl Phosphate

Quantities Taken: 13.38 mg. of Platinum and 7.40 mg. of Rhodium

Tube Number	Run #1		Run #2		Run #3		Run #4	
	mg. Rh	mg. Pt	mg. Rh	mg. Pt	mg. Rh	mg. Pt	mg. Rh	mg. Pt
0	7.24	0.00	7.56	0.00	7.40	0.00	7.30	0.00
1	0.20	0.00	tr	0.00	tr	0.00	tr	0.00
2	0.00	0.00	0.00	1.44	0.00	0.70	0.00	0.90
3	0.00	2.90	0.00	2.04	0.00	2.50	0.00	2.20
4	0.00	5.26	0.00	5.42	0.00	5.62	0.00	5.40
5	0.00	4.10	0.00	4.02	0.00	3.98	0.00	4.80

Average Recovery of Rhodium = 7.42 mg.

Average Recovery of Platinum = 12.64 mg.

TABLE XVI

Theoretical Data for the Separation of Platinum and Rhodium

Rhodium Data

n	$\left(\frac{1}{K_d + 1}\right)^n$	R	$K_d{}^R$	$\frac{n!}{R!\ (n - R)!}$	T_n	*mg. Rh Present
5	4.70×10^{-1}	0	1.00	1	0.47	3.48
		1	1.60×10^{-1}	5	0.38	2.81
		2	2.56×10^{-2}	10	0.12	0.89
		3	4.09×10^{-3}	10	0.02	0.15
		4	6.54×10^{-4}	5	0.00	0.00
		5	1.05×10^{-4}	1	0.00	0.00

* Based on 7.40 mg. Rhodium Taken for Separation

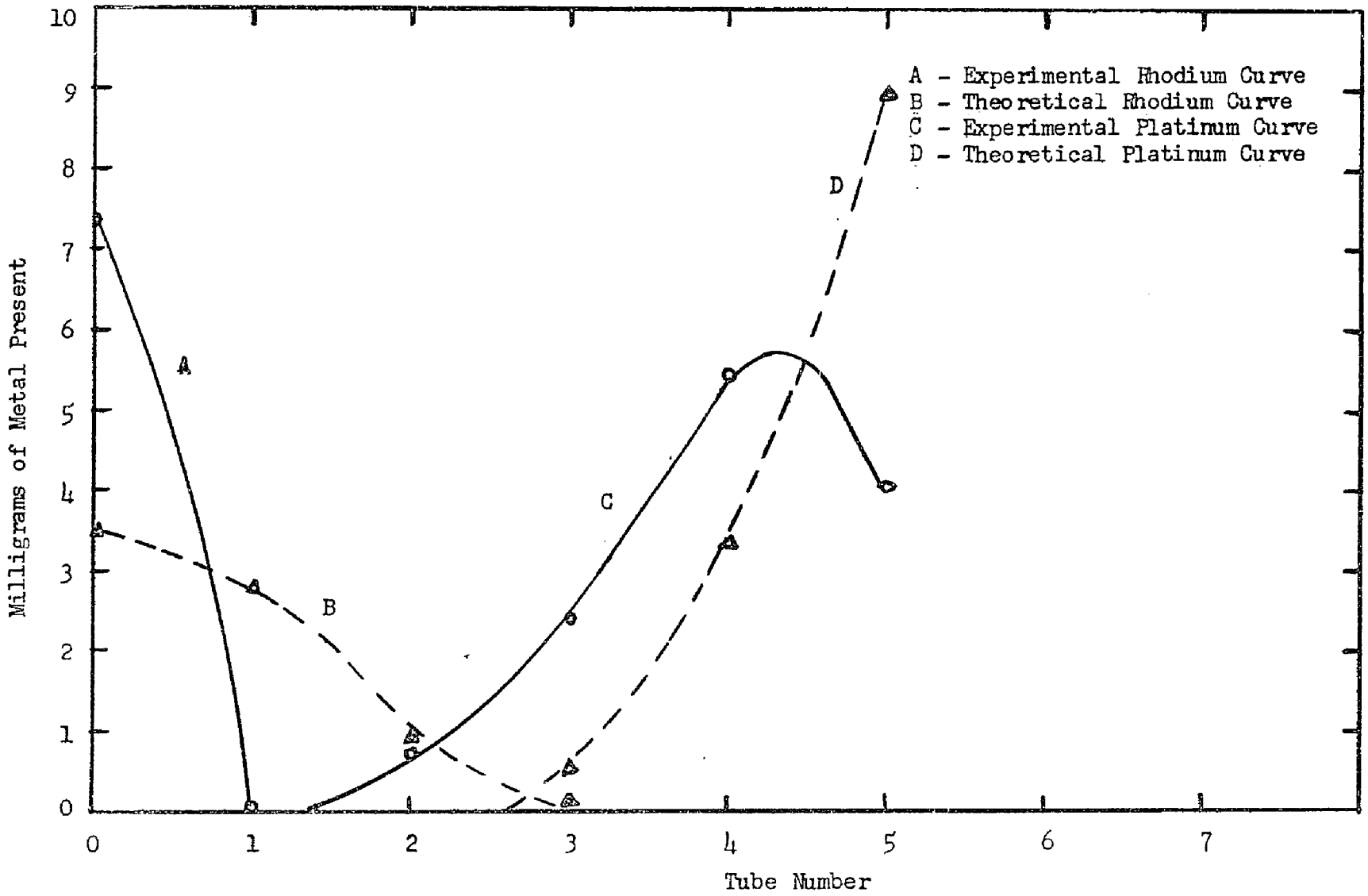
Platinum Data

n	$\left(\frac{1}{K_d + 1}\right)^n$	R	$K_d{}^R$	$\frac{n!}{R!\ (n - R)!}$	T_n	*mg. Pt Present
5	1.68×10^{-6}	0	1.00	1	0.00	0.00
		1	1.32×10	5	0.00	0.00
		2	1.74×10^{2}	10	0.00	0.00
		3	2.30×10^{3}	10	0.04	0.54
		4	3.03×10^{4}	5	0.25	3.35
		5	4.00×10^{5}	1	0.67	8.96

* Based on 13.38 mg. of Platinum Taken for Separation

FIGURE XI

Distribution Curves for the Separation of Rhodium and Platinum



(G) Separation of Platinum and Palladium

(1) Theoretical Section

The theory of countercurrent distribution was discussed in the theoretical section of the separation of rhodium and platinum. Therefore it will be omitted here.

(2) Experimental Section

In the separation of platinum and palladium, 10.00 ml. aliquots of a 1337 ppm. platinum stock solution and of a 1000 ppm. palladium stock solution were taken for separation. The standardized procedure was as follows:

The sample containing the mixture of platinum and palladium was evaporated to dryness on a steam bath. The residue was dissolved in 3M hydrochloric acid saturated with sodium chloride and tributyl phosphate. The sample solution was heated for ten minutes on a steam bath, cooled and transferred to tube 0 in the countercurrent extraction apparatus. The other tubes in the countercurrent extractor were filled with the raffinate, 3M hydrochloric acid saturated with sodium chloride and tributyl phosphate. Then 18 ml. of tributyl phosphate were added to tube 0. The system was equilibrated by inverting the tube and then allowing the system to settle. This was repeated twenty times. The extractant from tube 0 was then transferred to tube 1 and fresh extractant added to tube 0. This procedure was repeated until the initial aliquot of extractant was transferred to tube 16. The raffinate fraction from each tube was

combined with the strippings of their respective extractant phases. The analyses were then carried out as outlined in the Analytical Section.

(3) Results Section

The separation was run four times using the previously described procedure. The data for the four separations can be seen in tables XVII and XVIII. The theoretical data are given in tables XIX and XX. A plot of amount of metal against tube number is shown in figure XII. The solid lines represent the experimental values. The average recovery of platinum was 12.98 mg. of the 13.38 mg. taken and of palladium, 9.30 of the 10.00 mg. taken.

TABLE XVII

Data for the Separation of Platinum and Palladium

System: Hydrochloric Acid-Sodium Chloride-Tributyl Phosphate

Quantities Taken: 13.38 mg. of Platinum and 10.00 mg. of Palladium

	Run #1		Run #2	
Tube Number	mg. Pd	mg. Pt	mg. Pd	mg. Pt
0	0.00	0.00	0.00	0.00
1	tr	0.00	0.00	0.00
2	0.36	0.00	tr	0.00
3	0.82	0.00	0.36	0.00
4	1.46	0.00	0.90	0.00
5	1.82	0.00	1.52	0.00
6	1.78	0.00	1.90	0.00
7	1.56	0.00	2.00	0.00
8	0.90	0.00	1.58	0.00
9	0.46	0.00	1.08	0.00
10	0.00	0.40	tr	0.90
11	0.00	0.84	0.00	1.06
12	0.00	1.56	0.00	1.72
13	0.00	2.30	0.00	2.88
14	0.00	3.10	0.00	2.92
15	0.00	2.76	0.00	2.42
16	0.00	2.02	0.00	1.22

TABLE XVIII

Data for the Separation of Platinum and Palladium

System: Hydrochloric Acid-Sodium Chloride-Tributyl Phosphate

Quantities Taken: 13.38 mg. of Platinum and 10.00 mg. of Palladium

Tube Number	Run #3		Run #4	
	mg. Pd	mg. Pt	mg. Pd	mg. Pt
0	0.00	0.00	0.00	0.00
1	0.00	0.00	0.00	0.00
2	0.36	0.00	0.44	0.00
3	0.58	0.00	0.48	0.00
4	1.02	0.00	1.00	0.00
5	1.60	0.00	1.48	0.00
6	1.98	0.00	1.82	0.00
7	1.90	0.00	1.76	0.00
8	1.40	0.00	1.24	0.00
9	0.92	0.00	0.70	0.00
10	0.00	0.70	tr	0.96
11	0.00	1.56	0.00	1.46
12	0.00	2.10	0.00	1.98
13	0.00	3.16	0.00	2.90
14	0.00	2.70	0.00	2.90
15	0.00	1.70	0.00	1.60
16	0.00	1.00	0.00	1.08

Average Recovery of Platinum = 12.98 mg.

Average Recovery of Palladium = 9.30 mg.

TABLE XIX

Theoretical Data for the Separation of Platimum and Palladium

Palladium Data

n	$\left(\frac{1}{Kd + 1}\right)^n$	R	Kd^R	$\frac{n!}{R!\ (n - R)!}$	T_n	*mg. Pd Present
16	7.99×10^{-3}	0	1.00	1.00	0.00	0.00
		1	3.50×10^{-1}	1.60×10	0.04	0.40
		2	1.23×10^{-1}	1.20×10^{2}	0.12	1.20
		3	4.30×10^{-2}	5.60×10^{2}	0.19	1.90
		4	1.51×10^{-2}	1.82×10^{3}	0.22	2.20
		5	5.29×10^{-3}	4.37×10^{3}	0.18	1.80
		6	1.85×10^{-3}	8.01×10^{3}	0.12	1.20
		7	6.47×10^{-4}	1.14×10^{4}	0.06	0.60
		8	2.26×10^{-4}	1.29×10^{4}	0.02	0.20
		9	7.91×10^{-5}	1.14×10^{4}	0.00	0.00
		10	2.77×10^{-5}	8.01×10^{3}	0.00	0.00
		11	9.96×10^{-6}	4.37×10^{3}	0.00	0.00
		12	3.39×10^{-6}	1.82×10^{3}	0.00	0.00
		13	1.19×10^{-6}	5.60×10^{2}	0.00	0.00
		14	4.16×10^{-7}	1.20×10^{2}	0.00	0.00
		15	1.46×10^{-7}	1.60×10	0.00	0.00
		16	5.11×10^{-8}	1.00	0.00	0.00

* Based on 10.00 mg. of Palladium Taken for Separation

TABLE XX

Theoretical Data for the Separation of Platinum and Palladium

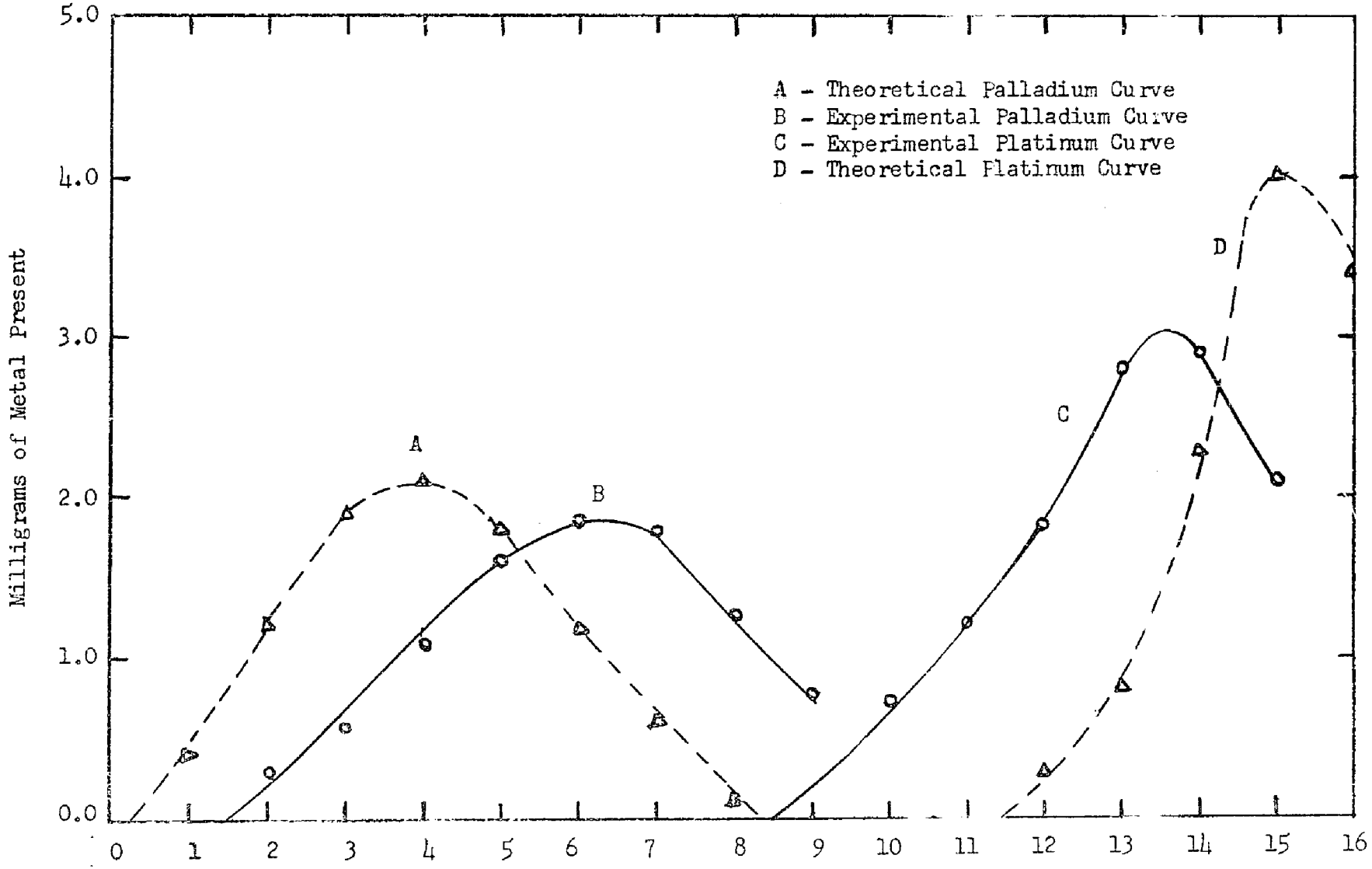
Platinum Data

n	$\left(\frac{1}{K_d + 1}\right)^n$	R	K_d^R	$\frac{n!}{R!\,(n-R)!}$	T_n	*mg. Pt Present
16	3.31×10^{-19}	0	1.00	1.00	0.00	0.00
		1	1.32×10	1.60×10	0.00	0.00
		2	1.74×10^2	1.20×10^2	0.00	0.00
		3	2.30×10^3	5.60×10^2	0.00	0.00
		4	3.03×10^4	1.82×10^3	0.00	0.00
		5	4.00×10^5	4.37×10^3	0.00	0.00
		6	5.28×10^6	8.01×10^3	0.00	0.00
		7	6.91×10^7	1.14×10^4	0.00	0.00
		8	9.12×10^8	1.29×10^4	0.00	0.00
		9	1.20×10^{10}	1.14×10^4	0.00	0.00
		10	1.58×10^{11}	8.01×10^3	0.00	0.00
		11	2.08×10^{12}	4.37×10^3	0.00	0.00
		12	2.74×10^{13}	1.82×10^3	0.02	0.27
		13	3.26×10^{14}	5.60×10^2	0.06	0.80
		14	4.30×10^{15}	1.20×10^2	0.17	2.28
		15	5.68×10^{16}	1.60×10	0.30	4.02
		16	7.50×10^{17}	1.00	0.25	3.35

* Based on 13.38 mg. of Platinum Taken for Separation

FIGURE XII

Distribution Curves for the Separation of Platinum and Palladium



DISCUSSION

The application of countercurrent distribution techniques to the problems of separations in the platinum group metals was a fresh approach to an old problem. The facility with which the separations were affected should do much toward encouraging the development of similar type separations.

A point for discussion, in the extraction of platinum, palladium, rhodium and iridium as the chlorides, is the type of species extracted. According to theory the most probable extracting species would be an uncharged one. Using iridium (IV) as an example several possible extraction mechanisms might be outlined.

(a) The formation of an undissociated acid which extracts

$$\underset{\text{Raffinate}}{Ir^{4+} + 6\ Cl^{-} \rightleftharpoons [Ir(Cl)_6]^{=} + 2\ H^{+} \rightleftharpoons H_2[Ir(Cl)_6]} \;\Big|\; \underset{\text{Extractant}}{\rightleftharpoons H_2[Ir(Cl)_6]}$$

(b) The formation of an uncharged complex

$$\underset{\text{Raffinate}}{Ir^{4+} + 4\ Cl^{-} \rightleftharpoons IrCl_4} \;\Big|\; \underset{\text{Extractant}}{\rightleftharpoons IrCl_4}$$

Considering the two situations, (a) appears to be the more probable for two reasons. First the variation of the distribution coefficient with hydrochloric acid concentration reflects more of a dependancy than (b) indicates. Also the stability of the $[Ir(Cl)_6]^{=}$ complex is

such as to almost preclude the formation of $IrCl_4$. Similar situations exist in the cases of the three other metals studied.

The role of the solvents in extraction procedures is also important. In many cases water of hydration has been an important factor affecting the distribution coefficient. Tributyl phosphate possesses an appreciable dipole moment and, with an exposed oxygen atom is quite capable of hydrogen bonding. If any water of hydration is associated with the complex there are two possible interactions. First the complex may extract into tributyl phosphate with the water of hydration interacting with the tributyl phosphate through hydrogen bonding phenomena. Also there is the possibility that the tributyl phosphate displaces the water of hydration and actually takes its place. These forces would be of the order of magnitude of ion-dipole forces. The effect of this dipolar interaction was qualitatively observed by decreasing the dielectric constant of the tributyl phosphate phase through the use of diluents (CCl_4, $CHCl_3$) which decreased the distribution coefficients appreciably. Other than to focus the attention on situation (a) and show that dipolar effects are important, no conclusions were drawn as to the exact structure of the extracting complex.

The extraction of the thiocyanate complexes posed the same problems as the chloride system along with two extra complications. In this system the thiocyanate complexes are formed at the expense of the chloride complexes, which means another equilibrium must be considered. Also in the case of iridium (IV) there is a possibility of

an oxidation-reduction reaction:

$$SCN^- \rightleftharpoons 1/2\ (SCN)_2 + e^- \qquad E^o = -0.77$$

$$[Ir(Cl)_6]^{=} + e^- \rightleftharpoons [Ir(Cl)_6]^{\equiv} \qquad E^o = +1.02$$

Hence $SCN^- + [Ir(Cl)_6]^{=} \rightleftharpoons [Ir(Cl)_6]^{\equiv} + 1/2\ (SCN)_2 \qquad E^o_{298} = +0.25$

$$\Delta F = -nFE$$

$$\Delta F = -5{,}766 \text{ cal./mole}$$

The possibility of shifting the equilibrium by extracting the thiocyanogen formed into the tributyl phosphate must also be considered. Qualitative tests in the laboratory disclosed that a purplish-red color was always extracted when iridium was present even though no iridium was extracted. Infra-red spectra could not be secured as of this date because the infra-red spectrometer was not functioning and adequate cells were not available. The dipolar interaction in the case of the thiocyanate system however was very small. Diluting the tributyl phosphate did not appreciably alter the distribution coefficient.

The choice of working with the chloride system was motivated by the preceding comparison. The only separations possible utilizing the thiocyanate system that could not be performed easily by the chloride system were the separation of rhodium and iridium and the separation of platinum and iridium. However the erratic behavior of iridium in the thiocyanate system makes the system a poor choice for any separation involving iridium. The attempt to separate rhodium and iridium was made in order to try to eliminate the manual procedure dictated by the oxidation steps required in the chloride system. In spite of the favorable difference in distribution coefficients

in the 500:1 thiocyanate to metal system, the rhodium and iridium were not resolved even after 11 stages on the countercurrent extractor.

The separation of rhodium and iridium in the chloride system was first attempted on the countercurrent extractor. The results showed a separation of part of the iridium from the rhodium. However the iridium remaining with the rhodium could not be extracted. Upon addition of hydrogen peroxide and boiling, the residual iridium could be extracted. This peculiar behavior can perhaps be attributed to two possibilities. First, part of the iridium (IV) may be reduced to iridium (III). The most likely source of the reducing agent was in the tributyl phosphate. In order to purify the tributyl phosphate, it was oxidized with potassium permanganate and vacuum distilled twice, the fraction coming over at 147-150° C. at 8 mm. pressure being collected. Using this tributyl phosphate as the extractant the residual iridium effect persisted. The other possibility was that the iridium (IV) or (III) existed as a different species and, since iridium complexes are of the inner orbital type, required drastic conditions in order to form the extractable species. Regardless of the nature of the chemical change it was necessary to include this "oxidation step" in the separational procedure. As a result of this step the procedure instituted was a manual one.

The separations of rhodium and platinum and of palladium and platinum were carried out on the countercurrent extractor as outlined in the Theoretical Section on countercurrent extraction.

The selection of experimental conditions was based on the largest difference in distribution coefficients concomitant with minimal reagent concentrations necessary.

Due to the fact that nitrate interferes with the extraction of the chlorides, it was necessary to vacuum distill the stripped tributyl phosphate in the solvent recovery process.

The separations affected are simple, fast and economical. These types of separations work very nicely on a laboratory scale and would probably not suffer much if extended to industrial use.

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VITA

William Lambert Senn, Jr. was born in Alexandria, Louisiana, on January 28, 1932. His early education took place in the Alexandria public schools. He graduated from Istrouma High School in Baton Rouge, Louisiana, in June, 1949, receiving a scholastic scholarship to Louisiana State University.

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Title of Thesis: EXTRACTION STUDIES IN THE PLATINUM METALS GROUP

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